DENSITY FUNCTIONAL CALCULATIONS NEAR FERROMAGNETIC QUANTUM CRITICAL POINTS

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Abstract   We discuss the application of the density functional theory in the local density approximation (LDA) near a ferromagnetic quantum critical point. The LDA fails to describe the critical fluctuations in this regime. This provides a fingerprint of a materials near ferromagnetic quantum critical points: overestimation of the tendency to magnetism in the local density approximation. This is in contrast to the typical, but not universal, tendency of the LDA to underestimate the tendency to magnetism in strongly Hubbard correlated materials. We propose a method for correcting the local density calculations by including critical spin fluctuations. This is based on (1) Landau expansion for the free energy, evaluated within the LDA, (2) lowest order expansion of the RPA susceptibility in LDA and (3) extraction of the amplitude of the relevant (critical) fluctuations by applying the fluctuation-dissipation theorem to the difference between a quantum-critical system and a reference system removed from the quantum critical point. We illustrate some of the aspects of this by the cases of Ni_3Al and Ni_3Ga, which are very similar metals on opposite sides of a ferromagnetic quantum critical point. LDA calculations predict that Ni_3Ga is the more magnetic system, but we find that due to differences in the band structure, fluctuation effects are larger in Ni_3Ga, explaining the fact that experimentally it is the less magnetic of the two materials.

Keywords: quantum criticality, magnetism, density functional theory, first-principles calculation.

1.   Introduction

Recent low temperature experiments on clean materials near ferromagnetic quantum critical points (FQCP) have revealed a remarkable range of unusual properties, including non-Fermi liquid scalings over a large phase space, unusual transport, and novel quantum ground states, particularly coexisting ferromagnetism and superconductivity in some materials. Although criticality usually implies a certain universality, present experiments show considerable

material dependent aspects that are not well understood, [1] *e.g.* the differences between UGe_2 and URhGe [2, 3] and $ZrZn_2$, [4] which both show coexisting ferromagnetism and superconductivity but very different phase diagrams, in contrast to MnSi, where very clean samples show no hint of superconductivity around the QCP, possibly because of the lack of the inversion symmetry. [5]

Moreover, by far not every magnetic material can be driven to a QCP by pressure or by other means of supressing ferromagnetism. Typically, the transition becomes first order as the Curie temperature, T_C is depressed. If this happens too far away from the fluctuation dominated regime, nothing interesting is seen. Also, more pedestrian effects are often important. For example, impurities or other defects can lead to scattering that smears out the quantum critical region.

2. The LDA Description Near a FQCP

One of the fingerprints of a FQCP, maybe the most universal one, is a substantial overestimation of the tendency to magnetism in conventional density functional theory (DFT) calculations, such as within the local density approximation (LDA). Generally, approaches based on density functional theory (DFT) are successful in accounting for material dependence in cases where sufficiently accurate approximations exist. Density functional theory is in principle an exact ground state theory. It should, therefore, correctly describe the spin density of magnetic systems. This is usually the case in actual state of the art density functional calculations. However, common approximations to the exact density functional theory, such as the LDA, may miss important physics and indeed fail to describe some materials. A well know example is in strongly Hubbard correlated systems, where the LDA treats the correlations in an orbitally averaged mean field way and often underestimates the tendency towards magnetism.

Overestimates of magnetic tendencies, especially in the LDA, are considerably less common, the exceptions being materials near magnetic quantum critical points (QCP); here the error comes from neglect of low energy quantum spin fluctuations. In particular, the LDA is parameterized based on the uniform electron gas at densities typical for atoms and solids. However, the uniform electron gas at these densities is stiff against magnetic degrees of freedom and far from magnetic QCP's. Thus, although the LDA is exact for the uniform electron gas, and therefore does include all fluctuation effects there, its description of magnetic ground states in solids and molecules is mean field like. This leads to problems such as the incorrect description of singlet states in molecules with magnetic ions as well as errors in solids when spin fluctuation effects beyond the mean field are important. In solids near a QCP, the result is an overestimate of the magnetic moments and tendency toward magnetism (*i.e.*

Table 1. Some materials near a FQCP that we have investigated by LDA calculations. Type 1 materials are ferromagnetic both in the calculations and in experiment; magnetic moments in μ_B per formula unit are given. Type 2 are ferromagnetic only in the calculations (calculated moments given, and type 3 are paramagnetic (susceptibility in 10^{-4}emu/mol is given). The references are to the LDA calculations.

Material	$ZrZn_2$	Ni_3Al	Sc_3In	FeAl	Ni_3Ga
Type	1	1	1	2	2
Calc/Exp	0.72/0.17	0.71/0.23	1.05/0.20	0.80	0.79
Ref.	[16]	[17]	[18]	[19]	[17]

Material	$Sr_3Ru_2O_7$	$SrRhO_3$	$Na_{0.5}CoO_2$	Pd
Type	2	2	2	3
Calc/Exp	0.80	0.9	0.5	11.6/6.8
Ref.	[8]	[20]	[10]	[21]

misplacement of the position of the critical point) due to neglect of the quantum critical fluctuations. [6, 7] Examples include three types of materials: paramagnets that are ferromagnetic in the LDA, ferromagnets where the equilibrium magnetic moment is substantially overestimated in the LDA, and paramagnets where the paramagnetic susceptibility is substantially overestimated.

We list examples of materials in all three categories in Table 1. At least two of these are cases where a large deviation between the LDA and experimental magnetic properties were noted, followed by transport measurements that suggest a nearby ferromagnetic quantum critical point. In particular, in $Sr_3Ru_2O_7$, LDA calculations with the experimental crystal structure found a sizeable moment, [8] while experimentally the material was known to be a paramagnetic metal. Grigera and co-workers then showed that $Sr_3Ru_2O_7$ has a metamagnetic quantum critical point at moderate field. [9] Pd metal provides another example: the calculated LDA magnetic susceptibility is nearly twice larger that the experimental one. Correspondingly, Nicklas *et al*[11] found a FQCP in the $Pd_{1-x}Ni_x$ system at $x = 0.026$, where the transport properties become non-Fermi liquid.

We emphasize that substantial overestimates of the tendency of metals towards ferromagnetism within the LDA is a rare occurance, and propose that it be used as an indicator of critical fluctuations in a material. However, for this to be an effective screen, competing states, like antiferromagnetism need to be ruled out in each material. An interesting case study is LiV_2O_4, which is a paramagnetic metal and occurs in the cubic spinel structure. Remarkably, it was discovered by Kondo and co-workers that this material behaves at low temperature like a heavy fermion metal. [12] LDA calculations showed that the material is unstable against ferromagnetism with a sizeable moment. [14, 15, 13] But calculations also show that the interactions are antiferromagnetic,

and as a result it is more unstable against antiferromagnetism, which however is frustrated on the spinel lattice. While LiV_2O_4 may be near an antiferromagnetic QCP, it is not a material near an FQCP.

3. "Beyond-LDA" Critical Fluctuations

A popular way to add quantum or termal fluctuation to a mean-field type theory is *via* fluctuation corrections to Ginzburg-Landau expansion of the free energy. For a detailed discussion we refer the reader to the book of Moriya [22] and the review article of Shimizu [23]. In short, one writes the free energy (or the magnetic field) as a function of the ferromagnetic magnetization, M,

$$E_{static}(M) = a_0 + \sum_{n\geq 1}\frac{1}{2n}a_{2n}M^{2n}, \tag{1}$$

$$H_{static}(M) = \sum_{n\geq 1}a_{2n}M^{2n-1} \tag{2}$$

(obviously, a_2 gives the inverse spin susceptibility without fluctuations), and then assume Gaussian zero-point fluctuations of an r.m.s. magnitude ξ for each of the d components of the magnetic moment (for a 3D isotropic material like Pd, $d = 3$). After averaging over the spin fluctuations, one obtains a fluctuation-corrected functional. The general expression can be written in the following compact form:

$$H(M) = \sum_{n\geq 1}\tilde{a}_{2n}M^{2n-1}$$

$$\tilde{a}_{2n} = \sum_{i\geq 0}C_{n+i-1}^{n-1}a_{2(n+i)}\xi^{2i}\Pi_{k=n}^{n+i-1}(1+\frac{2k}{d}). \tag{3}$$

For instance,

$$\tilde{a}_2 = a_2 + \frac{5}{3}a_4\xi^2 + \frac{35}{9}a_6\xi^4 + \frac{35}{3}a_8\xi^6...$$

$$\tilde{a}_4 = a_4 + \frac{14}{3}a_6\xi^2 + 21a_8\xi^6...$$

$$... \tag{4}$$

The unrenormalized coefficients can be taken from fixed spin momen LDA calculations, in which case ξ becomes the amplitude of those fluctuations only, which are not taken into account in LDA (as mentioned, LDA includes some quantum fluctuation, specifically short-range fluctuations present in the interacting uniform electron gas). In principle, one can estimate ξ from the fluctuation-dissipation theorem, which states that (see, e.g., Refs. [24, 25])

$$\xi^2 = \frac{4\hbar}{\Omega}\int d^3q \int \frac{d\omega}{2\pi}\frac{1}{2}\operatorname{Im}\chi(\mathbf{q},\omega), \tag{5}$$

where $\chi(\mathbf{q}, \omega)$ is the magnetic susceptibility and Ω is the Brillouin zone volume. It is customary to approximate $\chi(\mathbf{q}, \omega)$ by its small q, small ω expansion [24, 25]:

$$\chi_0(\mathbf{q}, \omega) = N(E_F) - aq^2 + ib\omega/q \tag{6}$$

$$\chi^{-1}(\mathbf{q}, \omega) = \chi_0^{-1}(\mathbf{q}, \omega) - I, \tag{7}$$

With the expansion (6) the integrations can be performed analytically, and the final result reads:

$$\xi^2 = \frac{bv_F^2 N(E_F)^2}{2a^2\Omega}[Q^4 \ln(1 + Q^{-4}) + \ln(1 + Q^4)]. \tag{8}$$

where $Q = q_c\sqrt{a/bv_F}$, and q_c is the cutoff parameter for momentum integration in Eqn. 5 (the frequency integration at a given q is usually assumed to be cut off at $\omega = v_F q$).

To proceed along these lines one needs to find a way to calculate the crucial parameters of the expansion (6). It was suggested by Moriya [22] that these can be expressed as certain integrals over the Fermi surface, by expanding the RPA expression for χ_0. Below, we offer a derivation equivalent to that of Moriya, but rendering the results in more computable form. We start with the RPA expressions for the real and imaginary parts of χ_0 :

$$\mathrm{Re}\,\chi_0(\mathbf{q}, 0) = \sum_{\mathbf{k}} [f(E_{\mathbf{k}}) - f(E_{\mathbf{k}+\mathbf{q}})](E_{\mathbf{k}+\mathbf{q}} - E_{\mathbf{k}})^{-1} \tag{9}$$

$$\mathrm{Im}\,\chi_0(\mathbf{q}, \omega) = \sum_{\mathbf{k}} [f(E_{\mathbf{k}}) - f(E_{\mathbf{k}+\mathbf{q}})]\delta(E_{\mathbf{k}+\mathbf{q}} - E_{\mathbf{k}} - \omega), \tag{10}$$

where $f(E)$ is the Fermi function, $-\frac{df(E)}{dE} = \delta(E - E_F)$. Expanding Eqn. 9 in $\Delta = E_{\mathbf{k}+\mathbf{q}} - E_{\mathbf{k}} = \mathbf{v_k}{\cdot}\mathbf{q} + \frac{1}{2}\sum_{\alpha\beta}\mu_{\mathbf{k}}^{\alpha\beta}q_\alpha q_\beta + ...$, we get to second order in q

$$\mathrm{Re}\,\chi_0(\mathbf{q}, \mathbf{0}) = N(E_F) + \sum_{\mathbf{k}}[\frac{1}{2}\left(\frac{d\delta(\varepsilon_{\mathbf{k}} - E_F)}{dE_F}\right)(\mathbf{v_k}{\cdot}\mathbf{q} + \frac{1}{2}\sum_{\alpha,\beta}\mu_{\mathbf{k}}^{\alpha\beta}q_\alpha q_\beta)$$

$$+\frac{1}{6}\left(\frac{d^2\delta(\varepsilon_{\mathbf{k}} - E_F)}{dE_F^2}\right)(\mathbf{v_k}{\cdot}\mathbf{q})^2].$$

The odd powers of $\mathbf{v_k}$ cancel out and we get ($\alpha, \beta = x, y, z$)

$$\mathrm{Re}\,\chi_0(\mathbf{q}) =$$

$$N(E_F) + \sum_{\alpha,\beta}\frac{q_\alpha q_\beta}{4}\frac{d\left\langle N(E_F)\mu^{\alpha\beta}\right\rangle}{dE_F} + \sum_{\alpha,\beta}\frac{q_\alpha q_\beta}{6}\frac{d^2\left\langle N(E_F)v_\alpha v_\beta\right\rangle}{dE_F^2}$$

$$= N(E_F) + \frac{q^2}{4}\frac{d\left\langle N(E_F)\mu_{xx}\right\rangle}{dE_F} + \frac{q^2}{6}\frac{d^2\left\langle N(E_F)v_x^2\right\rangle}{dE_F^2},$$

6

where $v_x^2 = v_y^2 = v_z^2$, $\mu_{xx} = \mu_{yy} = \mu_{zz}$. The last equality assumes cubic symmetry; generalization to a lower symmetry is trivial. Using the following relation,

$$\sum_{\mathbf{k}} \nabla_{\mathbf{k}} F(\varepsilon_{\mathbf{k}}) = \sum_{\mathbf{k}} \frac{dF(\varepsilon_{\mathbf{k}})}{d\varepsilon_{\mathbf{k}}} \nabla_{\mathbf{k}} \cdot \varepsilon_{\mathbf{k}} = \sum_{\mathbf{k}} \frac{dF(\varepsilon_{\mathbf{k}})}{d\varepsilon_{\mathbf{k}}} \mathbf{v}_{\mathbf{k}},$$

one can prove that

$$\frac{d^2 \langle N(E_F)v_x^2 \rangle}{dE_F^2} = -\frac{d \langle N(E_F)\mu_{xx} \rangle}{dE_F}. \tag{11}$$

Therefore

$$\mathrm{Re}\,\chi_0(\mathbf{q}) = N(E_F) - \frac{q^2}{12} \frac{d^2 \langle N(E_F)v_x^2 \rangle}{dE_F^2} \tag{12}$$

Similarly, for Eqn. 10 one has

$$\mathrm{Im}\,\chi_0(\mathbf{q},\omega) = \sum_{\mathbf{k}} \left[\left(-\frac{df(\varepsilon)}{d\varepsilon} \right) \omega \delta(\mathbf{v}_{\mathbf{k}}\cdot\mathbf{q} - \omega) \right] \tag{13}$$

After averaging over the directions of $\mathbf{q}$, this becomes, for small ω,

$$\mathrm{Im}\,\chi_0(q,\omega) = \frac{\omega}{2} \sum_{\mathbf{k}} \frac{\delta(\varepsilon_{\mathbf{k}})}{v_{\mathbf{k}}q} \theta(v_{\mathbf{k}}q - \omega) = \frac{\omega}{2q} \left\langle N(E_F)v^{-1} \right\rangle$$

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2}. \tag{14}$$

Although in real materials the Fermi velocity is obviously different along different directions, it is still a reasonable approximation to introduce an average v_F. Then the above formulae reduce all parameters needed for estimating the *r.m.s.* amplitude of the spin fluctuations to four integrals over the Fermi surface, specifically, the density of states, $N(E_F)$, $a = \frac{1}{12} \frac{d^2 \langle N(E_F)v_x^2 \rangle}{dE_F^2}$, $b = \frac{1}{2} \left\langle N(E_F)v^{-1} \right\rangle$ and $v_F = \sqrt{3 \frac{\langle N(E_F)v_x^2 \rangle}{N(E_F)}}$.

The physical meaning of these parameters is as follows. a defines the rate at which the static susceptibility $\chi(q,0)$ falls away from the zone center, *i.e.* the extent to which the tendency to ferromagnetism is stronger than that to antiferromagnetism. This translates into the phase space in the Brillouin zone where the spin fluctuations are important. b controls the dynamic effects in spin susceptibility.

Note that the cutoff parameter q_c remains the only undefined quantity in this formalism. One obvious choice is $q_c = \sqrt{N(E_F)/a}$, because for larger q the approximation (6) gives unphysical negative values for the static susceptibility.
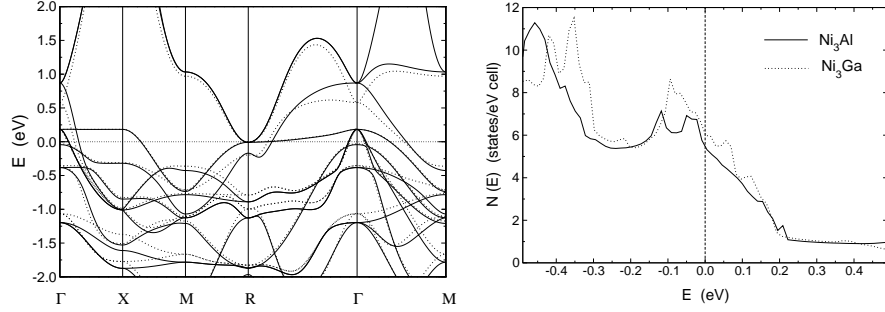
Figure 1. Calculated LDA band structure (left) and density of states (right) per f.u. for non-spin-polarized Ni$_3$Al (solid lines) and Ni$_3$Ga (dotted lines). E_F is at 0 eV.

On the other hand, one may argue that q_c should reflect mainly the geometry of the Fermi surface and thus not depend on a at all. We will come back to this issue later in this paper and will propose an approach that avoids using q_c whatsoever.

4.   Ni$_3$Al and Ni$_3$Ga

Here we use the closely related compounds Ni$_3$Al and Ni$_3$Ga to illustrate some of the above ideas. Further details may be found in Ref. [17]. These have the ideal cubic Cu$_3$Au $cP4$ structure, with very similar lattice constants, $a = 3.568$ A and $a = 3.576$ A, respectively, and have been extensively studied by various experimental techniques. Ni$_3$Al is a weak itinerant ferromagnet, $T_c = 41.5$ K and magnetization, M=0.23 μ_B/cell (0.077 μ_B/Ni atom) [26] with a QCP under pressure at P_c=8.1 GPa, [27] while Ni$_3$Ga is a strongly renormalized paramagnet. [28] Further, it was recently reported that Ni$_3$Al shows non-Fermi liquid transport over a large range of P and T range down to very low T. [29]

Previous LDA calculations showed that the magnetic tendency of both materials is overestimated within the LDA, and that Ni$_3$Ga is incorrectly predicted to be a ferromagnet. [30–35] Moreover, in the LDA the tendency to magnetism is stronger in Ni$_3$Ga than Ni$_3$Al, *opposite to the experimental trend.* This poses an additional challenge to any theory striving to describe the material dependent aspects of quantum criticality. The two materials are expected to be very similar electronically (the small difference between the two is due to relativistic effects associated with Ga in Ni$_3$Ga). Thus these two very similar metals offer a very useful and sensitive benchmark for theoretical approaches. We use this to test an approach based on the fluctuation dissipation theorem applied to the LDA band structures with an ansatz for the cut-off q_c. We find that this approach corrects the ordering of the magnetic tendencies of the materials, and

gives the right ground states at ambient pressure as well as a reasonable value of P_c for Ni$_3$Al.

The LDA calculations were done using the general potential linearized augmented planewave (LAPW) method with local orbital extensions [36, 37, 39] as decribed in Ref. [17], with the exchange-correlation functional of Hedin and Lundqvist with the von Barth-Hedin spin scaling [40, 41]. The LDA electronic structure is given in Fig. 1 and Table 2, while results of fixed spin moment calculations of the magnetic properties at the experimental lattice parameters and under hydrostatic compression are given in Figs. 2 and 3. The two compounds are very similar in both electronic and magnetic properties, the main apparent difference being the higher equilibrium moment of Ni$_3$Ga (0.79 μ_B/f.u. *vs.* 0.71 μ_B/f.u.), in agreement with other full potential calculations. [34, 35]

The propensity towards magnetism may be described in terms of the Stoner criterion, $IN(E_F)$, where I is the so-called Stoner parameter, which derives from Hund's rule coupling on the atoms. For finite magnetizations, the so-called extended Stoner model [42], states that, to the second order in the spin density, the magnetic stabilization energy is given by

$$\Delta E = M^2[\int_0^M m \ dm/2\tilde{N}(m) - I/4], \tag{15}$$

where $\tilde{N}(M)$ is the density of states averaged over the exchange splitting corresponding to the magnetization M. Fitting the fixed spin moment results to this expression, we find $I_{Al} = 0.385$ eV and $I_{Ga} = 0.363$ eV. These gives $IN(E_F) = 1.21$ and $IN(E_F) = 1.25$ for Ni$_3$Al and Ni$_3$Ga, respectively. Both numbers are larger than unity, corresponding to a ferromagnetic instability, and the value for Ni$_3$Ga is larger than that for Ni$_3$Al. Importantly, the difference comes from the density of states, since $I_{Al} > I_{Ga}$. In both compounds, magnetism is suppressed by compression, with an LDA critical point at a value $\delta a/a \sim$ -0.05 $-$ -0.06. In Ni$_3$Al, the critical point at $\delta a/a =$-0.058 corresponds to the pressure of $P_c =$50 GPa, [43] which is much higher than the experimental value. It is interesting that, as in ZrZn$_2$ [16], the exchange splitting is very strongly **k**-dependent; for instance, in Ni$_3$Al at some points it is as small as 40 meV/μ_B near the Fermi level, while at the others (of pure Ni d character) it is close to 220 meV/μ_B.

Notwithstanding the general similarity of the two compounds, there is one important difference near the Fermi level, specifically, the light band crossing the Fermi level in the middle of the Γ-M or Γ-X directions is steeper in Ni$_3$Al (Fig. 1). This, in turn, leads to smaller density of states. This comes from a different position of the top of this band at the Γ point, 0.56 eV in Ni$_3$Ga and 0.85 eV in Ni$_3$Al. The corresponding electronic state is a mixture of Ni p and Al (Ga) p states, and is the only state near the Fermi level with substantial Al (Ga) content. Due to relativistic effects, the Ga p level is lower than the
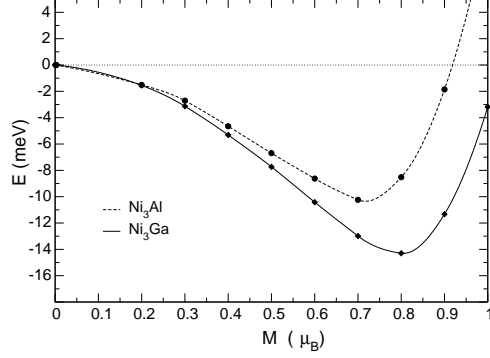
Figure 2. Energy *vs.* fixed spin moment for Ni$_3$Al and Ni$_3$Ga at the experimental lattice parameters. The energy zero is set to the non-spin-polarized value.

Table 2. Magnetic energy (see text), magnetic moment in μ_B/cell and $N(E_F)$ in eV^{-1} for Ni$_3$Al and Ni$_3$Ga on a per spin per formula unit basis.

	$|\Delta E|$ (meV)	M (calc.)	M(expt.)	$N(E_F)$
Ni$_3$Al	10.3	0.71	0.23	3.2
Ni$_3$Ga	14.3	0.79	0.00	3.4

Al p level and this leads to the difference in the position of the corresponding hybridized state. Note that this is a purely scalar relativistic effect. Including spin orbit does not produce any further discernible difference.

Returning to magnetism, the fixed spin moment calculations provide the energy E as a function of the magnetization M (Fig. 2). One can write a Landau expansion for $E(M)$ as in Eqn. 1, which may then be treated as a mean field expression adding the effects of spin fluctuations. [23]

Treating this as a mean field expression and adding the effects of spin fluctuations [23] leads to renormalization of the expansion coefficients. The renormalized coefficients $\tilde{a}_i$ are written as power series in the averaged square of the magnetic moment fluctuations beyond the LDA, ξ^2 as in Eqn. 3. ξ may then be estimated by requiring that the corrected Landau functional reproduces the experimental magnetic moment (for Ni$_3$Al) or experimental magnetic susceptibility (for Ni$_3$Ga). The "experimental" ξ's obtained in this manner are are 0.47 and 0.55, respectively, which implies that spin fluctuation effects must be stronger in Ni$_3$Ga than in Ni$_3$Al.

A link can now be made between this fact and the electronic structures, using the formalism outlined in the previous section. As discussed, the cutoff
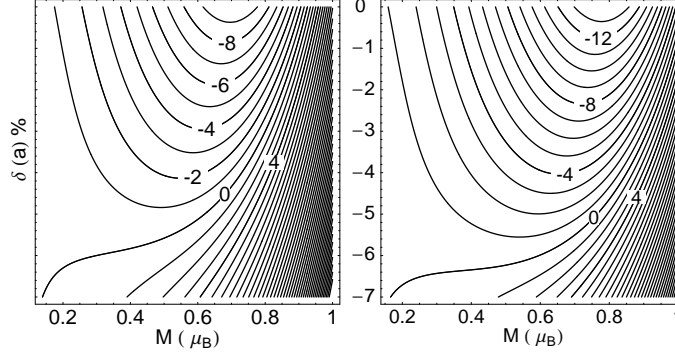
Figure 3.   FSM calculations under hydrostatic pressures. Magnetic energy, defined as the energy relative to the non-spin-polarized result at the same volume, as a function of the moment and linear compression. Left and right panels correspond to Ni_3Al and Ni_3Ga, respectively.

parameter q_c is the least well defined quantity in this formalism. Furthermore, the fermiology of these compounds is very complicated: in the paramagnetic state, there are four Fermi surfaces, two small and two large (one open and one closed). In this situation, it is hardly possible to justify any simple prescription for q_c. Therefore, we chose a different route: we assume that q_c is the *same* for both materials, and choose a number which yields a good description of both the equilibrium moment in Ni_3Al and the paramagnetic susceptibility in Ni_3Ga, $q_c = 0.382\ a_0^{-1}$. Note that this is larger that the diameters of the small Fermi surfaces but smaller than the radius of the Brillouin zone, $\approx 0.5\ a_0^{-1}$.

To calculate the above quantities, especially a, we need accurate values of the velocities on a fine mesh. Numerical differentiation of energies within the tetrahedron method proved to be too noisy. Therefore we use the velocities obtained analytically as matrix elements of the momentum operator, computed within the *optic* program of the WIEN package. A bootstrap method, [44] as described in Ref. [21], was used to obtain stable values for a, b. We found for Ni_3Al, using as the energy unit Ry, the length unit Bohr, and the velocity unit Ry·Bohr, $a = 230$, $b = 210$, $v_F = 0.20$, and $\xi = 0.445\ \mu_B$. For Ni_3Ga $a = 140$, $b = 270$, $v_F = 0.19$, and $\xi = 0.556\ \mu_B$. Using the resulting values of ξ each compound we obtain a magnetic moment of $M = 0.3\ \mu_B$/cell for Ni_3Al and a paramagnetic state with the renormalized susceptibility $\chi(0,0) = 1/\tilde{a}_2 = 6.8 \times 10^{-5}$ emu/g for Ni_3Ga, thus correcting the incorrect ordering of the magnetic tendencies of these two compounds and reproducing extremely well the experimental numbers of $M = 0.23\ \mu_B$, $\chi(0,0) = 6.7 \times 10^{-5}$ emu/g, respectively. This qualitative behavior is due to the different coefficient a, *i.e.*, different q dependencies of $\chi_0(q,0)$ at small q, which relates to the phase space available for soft fluctuations.

Now we turn to the pressure dependence. The above results imply that beyond-LDA fluctuations are already larger than the moments themselves at $P = 0$. In this regime, we may assume that the size of the beyond-LDA fluctuations is only weakly pressure dependent. Then we can apply Eqn. 3 to the data shown in Fig. 3 using $\xi = 0.47$ as needed to match the $P = 0$ value of M. This yields a value P_c=10 GPa in quite good agreement with the experimental value, P_c=8.1 GPa. [27]

5. Towards a Fully First Principles Theory

The results for Ni_3Al and Ni_3Ga, discussed above, and in Ref. [17], show that an approach based on correction of the LDA using the fluctuation dissipation theorem has promise. However, the results hinge on an unknown cut-off, which serves the purpose of including fluctuations that are associated with the FQCP and are not included in the LDA, from those that are included in the LDA. While it is apparently possible to obtain useful results using reasonable ansatz for this cut-off, it would be much better to have a truly first principles theory, with no parameters. In order to construct such a theory, one should find a way of solving the double counting problem, *i.e* including in the correction only those fluctuations that are not already taken into acount at the LDA level. This amounts to subtracting from Eqn. 5 the fluctuations already included in the LDA. Since the LDA is known to work well for materials far from an FQCP, this means that the correction should be zero or close to it for the most materials.

We suggest that a consistent way to accomplish this is by introducing a "reference" susceptibility $\chi^{ref}(\mathbf{q}, \omega)$ and subtracting it from $\chi(\mathbf{q}, \omega)$:

$$\xi^2 = \frac{4\hbar}{\Omega} \int d^3q \int \frac{d\omega}{2\pi} \frac{1}{2} \text{Im}[\chi(\mathbf{q}, \omega) - \chi^{ref}(\mathbf{q}, \omega)], \tag{16}$$

We shall use the same expansion6 for both $\chi(\mathbf{q}, \omega)$ and $\chi^{ref}(\mathbf{q}, \omega)$, to derive equivalent expansions

$$\chi^{-1}(\mathbf{q}, \omega) = \chi_0^{-1}(0, 0) - I + Aq^2 - iB\omega/q, \tag{17}$$

where $\chi_0^{-1}(0, 0) = 1/N(E_F)$ (density of states per spin) is the bare (non-interacting) static uniform susceptibility, and the Stoner parameter I is only weakly dependent on $\mathbf{q}$ and ω. Note that $A = a/N^2$, $B = b/N^2$, where a and b are the coefficients introduced in Eq.6. We also introduce a notation, $\Delta = N(E_F)^{-1} - I$. As long the same functional form (17) is used for $\chi(\mathbf{q}, \omega)$ and $\chi^{ref}(\mathbf{q}, \omega)$, the condition for the convergence of the integral (16) is that the coefficients A and B, controlling the short-range and high frequency fluctuations are the same. Of course, the parameter Δ, defining the proximity to the QCP, is different in the reference system, which like the uniform electron

gas upon which the LDA is based, should be far from any QCP (let us call Δ for the reference system Δ_0).

To calculate the integral ((16), we write it in the following form:

$$\xi^2 = \frac{4\hbar}{\Omega} \int d^3q \int \frac{d\omega}{2\pi} \frac{1}{2} \text{Im}[\chi(\Delta, \mathbf{q}, \omega) - \chi(\Delta_0, \mathbf{q}, \omega)]. \qquad (18)$$

For instance, $\chi(0, \mathbf{q}, \omega)$ represents the susceptibility right at the FQCP. This diverges for $\mathbf{q} = 0$, $\omega = 0$. The derivation then proceeds as follows:

$$\int^{\omega_c} d\omega \, \text{Im}[\chi(\Delta, q, \omega)] = \frac{q}{2B} \ln[\frac{(\Delta + Aq^2)^2 + B^2\omega_c^2/q^2}{(\Delta + Aq^2)^2}]. \qquad (19)$$

Where we introduce the Landau cutoff frequency, $\omega_c = vq$ (here v is an average Fermi velocity) and the notation $\beta = Bv$. We will also need the following function:

$$
\begin{aligned}
F(\Delta, \beta, x) &= \int x^3 dx \ln[(\Delta + x^2)^2 + \beta^2] \\
&= \frac{(\Delta + x^2)^2 + \beta^2}{4} \{\ln[(\Delta + x^2)^2 + \beta^2] - 1\} \\
&- \frac{\Delta(\Delta + x^2)}{2} \{\ln[(\Delta + x^2)^2 + \beta^2] - 2\} + \beta\Delta \tan^{-1} \frac{\beta}{\Delta + x^2}
\end{aligned}
$$

Now

$$
\begin{aligned}
\xi^2 &= \frac{2}{\Omega A^2 B} \lim_{Q \to \infty} [F(\Delta, \beta, Q) - F(\Delta_0, \beta, Q) \\
&- F(\Delta, 0, Q) + F(\Delta_0, 0, Q) - F(\Delta, \beta, 0) \\
&+ F(\Delta_0, \beta, 0) + F(\Delta, 0, 0) - F(\Delta_0, 0, 0)].
\end{aligned}
$$

This is particularly easy to evaluate at $\Delta = 0$. The result is

$$
\begin{aligned}
\Xi^2(\Delta_0) &= \\
\frac{2}{\Omega A^2 B} &[\Delta_0 \beta(\frac{\pi}{2} - \tan^{-1} \frac{\Delta_0}{\beta}) + \frac{\beta^2 - \Delta_0^2}{4} \ln \frac{\Delta_0^2 + \beta^2}{\beta^2} + \frac{\Delta_0^2}{4} \ln \frac{\Delta_0^2}{\beta^2}] \\
\Xi^2(S_0) &= \frac{N^2 bv_F^2}{2\Omega a^2} [4S_0 \tan^{-1}(S_0^{-1}) + \ln(1 + S_0^2) - S_0^2 \ln(1 + S_0^{-2})],
\end{aligned}
$$

where $S_0 = \Delta_0 N^2 / bv_F$. Obviously, for arbitrary Δ the answer is simply

$$\xi^2 = \Xi^2(S_0) - \Xi^2(S). \qquad (20)$$

Given that usually the reason for a quantum criticality is a large density of states, it makes sense to take the Stoner parameter for the reference system

the same as for the system in question. The point is that the density of states is a highly non-local parameter (note that it involves a delta function integral in energy), which can hardly be discerned from local information about the charge density, while the Stoner parameter is a very local quantity associated with the exchange-correlation potential. The difference between Δ and Δ_0 then comes from the difference between $N = N(E_F)$ and the density of states, N_0, of the reference system.

One may think about several different ways for choosing N_0. One may be to take average $N(E)$ over the width of the valence band, $N_0 = n/t$, where n is the total number of states in the band and t is its width. One can also think about the density of states of the uniform electron gas with the same Stoner parameter. There may be other, more sophisticated prescriptions. Probably, the most practical approach will be found after several trial and error tests with real materials.

6.   Summary and Open Questions

The failure of the usual approximations to density functional theory, for example, the LDA, to describe the magnetic properties of materials near ferromagnetic quantum critical points is associated with renormalization due to critical fluctuations. It is pointed out that since such fluctuations are invariably antagonistic to ferromagnetic ordering, deviations between experiment and LDA calculations in which the LDA is overly ferromagnetic can be a useful screen for materials near FQCPs. These errors in the LDA can be corrected using a phenomenalogical Landau function approach with the fluctuation amplitude as a parameter. However, there is hope that this parameter can be obtained from the electronic structure via the fluctuation dissipation theorem and a suitable reference system. The key remaining challenges in our view are to define the reference system to be used, and to use calculations to determine the usefulness of this approach for real materials near a critical point.

Acknowledgments

References

[1] R.B. Laughlin, G.G. Lonzarich, P. Monthoux and D. Pines, Adv. Phys. **50**, 361 (2001).

[2] S.S. Saxena, P. Agarwal, K. Ahilan, F.M. Grosche, R.K.W. Haselwimmer, M.J. Steiner, E. Pugh, I.R. Walker, S.R. Julian, P. Monthoux, G.G. Lonzarich, A. Huxley, I. Sheikin, D. Braithwaite, and J. Flouquet, Nature **406**, 587 (2000).

[3] D. Aoki, A. Huxley, E. Ressouche, D. Braithwaite, J. Flouquet, J.P. Brison, E. Lhotel, and C. Paulsen, Nature **413**, 613 (2001).

[4] C. Pfleiderer, M. Uhlarz, S.M. Hayden, R. Vollmer, H. von Lohneysen, N.R. Bernhoeft, and G.G. Lonzarich, Nature **412**, 58 (2001).

[5] C.P. Pfleiderer, S.R. Julian and G.G. Lonzarich, Nature **414**, 427 (2001).

[6] H. Yamada, K. Fukamichi and T. Goto, Phys. Rev. B **65**, 024413 (2001).

[7] A.J. Millis, A.J. Schofield, G.G. Lonzarich and S.A. Grigera, Phys. Rev. Lett. **88**, 217204 (2002).

[8] D.J. Singh and I.I. Mazin, Phys. Rev. B **63**, 165101 (2001).

[9] S.A. Grigera, R.S. Perry, A.J. Schofield, M. Chiao, S.R. Julian, G.G. Lonzarich, S.I. Ikeda, Y. Maeno, A.J. Millis, and A.P. Mackenzie, Science **294**, 329 (2001).

[10] D.J. Singh, Phys. Rev. B **61**, 13397 (2000); D.J. Singh, Phys. Rev. B **68**, 020503 (2003).

[11] M. Nicklas, M. Brando, G. Knebel, F. Mayr, W. Trinkl, and A. Loidl, Phys. Rev. Lett. **82**, 4268 (1999).

[12] S. Kondo, D.C. Johnston, C.A. Swenson, F. Borsa, A.V. Mahajan, L.L. Miller, T. Gu, A.I. Goldman, M.B. Maple, D.A. Gajewski, E.J. Freeman, N.R. Dilley, R.P. Dickey, J. Merrin, K. Kojima, G.M. Luke, Y.J. Uemura, O. Chmaissem and J.D. Jorgensen, Phys. Rev. Lett. **78**, 3729 (1997).

[13] D.J. Singh, P. Blaha, K. Schwarz, and I. I. Mazin, Phys. Rev. B **60**, 16359 (1999).

[14] V. Eyert, K.H. Hock, S. Horn, A. Loidl and P.S. Riseborough, Europhysics Lett. **46**, 762 (1999).

[15] V.I. Anisimov, M.A. Korotin, M. Zølfl, T. Pruschke, K. Le Hur and T.M. Rice, Phys. Rev. Lett. **83**, 364 (1999).

[16] D.J. Singh and I.I. Mazin, Phys. Rev. B **69**, 020402 (2004).

[17] A. Aguayo, I.I. Mazin, and D.J. Singh, cond-mat/0310629.

[18] A. Aguayo and D.J. Singh, Phys. Rev. B **66**, 020401 (2002).

[19] A.G. Petukhov, I.I.Mazin, L. Chioncel and A. I. Lichtenstein, Phys. Rev. B **67**, 153106 (2003).

[20] D.J. Singh, Phys. Rev. B **67**, 054507 (2003).

[21] P. Larson, I.I. Mazin and D.J. Singh, cond-mat/0305407 (Phys. Rev. B, January 2004, in press).

[22] T. Moriya, *Spin fluctuations in itinerant electron magnetism* (Berlin, Springer, 1985).

[23] M. Shimizu, Rep. Prog. Phys. **44**, 329 (1981).

[24] A.Z. Solontsov and D. Wagner, Phys. Rev. **B51**, 12410 (1995).

[25] S.N. Kaul, J. Phys. Cond. Mat. **11**, 7597 (1999).

[26] F.R. de Boer, C.J. Schinkel, J. Biesterbos, and S. Proost, J. Appl. Phys. **40**, 1049 (1969).

[27] P.G. Niklowitz, F. Beckers, N. Bernhoeft, D. Braithwaite, G. Knebel, B. Salce, J. Thomasson, J. Floquet and G.G. Lonzarich (unpublished); presented at Conference on Quantum Complexities in Condensed Matter, 2003.

[28] S.M. Hayden, G.G. Lonzarich and H.L. Skriver, Phys. Rev. B **33**, 4977 (1986).

[29] M.J. Steiner, F. Beckers, P.G. Nicklowitz and G.G. Lonzarich, Physica B **329**, 1079 (2003).

[30] J.J. Buiting, J. Klʉbler, and F.M. Mueller, J. Phys. F **39** L179 (1983).

[31] V.L. Moruzzi and P.M. Marcus, Phys. Rev. B, **42**, 5539 (1990).

[32] B.I. Min, A.J. Freeman, and H.J.F. Jansen, Phys. Rev. B **37**, 6757 (1988).

[33] J.H. Xu, B.I. Min, A.J. Freeman, and T. Oguchi, Phys. Rev. B **41**, 5010 (1990).

[34] G.Y Guo, Y.K. Wang, Li-Shing Hsu, J. Magn. Magn. Mater. **239**, 91 (2002).

[35] L.-S. Hsu, Y.-K. Wang and G.Y. Guo, J. Appl. Phys. **92**, 1419 (2002).

[36] D.J. Singh, *Planewaves Pseudopotentials and the LAPW Method* (Kluwer Academic, Boston, 1994).

[37] D. Singh, Phys. Rev. B **43**, 6388 (1991).

[38] S.H. Wei and H. Krakauer, Phys. Rev. Lett. **55**, 1200 (1985).

[39] P. Blaha, K. Schwarz G.K.H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2K, An Augmented Plane Wave + Local Orbitals Program for for Calculating Crystal Properties* (K. Schwarz, Techn. Universitat Wien, Austria, 2001), ISBN 3-9501031-1-2.

[40] L. Hedin and B. Lundqvist, J. Phys. C, **4**, 2064 (1971).

[41] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[42] G.L. Krasko, Phys. Rev. B, **36** 8565 (1987).

[43] To compute pressure, we used $P = B/B'[(V/V_0)^{B'} - 1]$, where V/V_0 is the volume compression, B and B' are the bulk modulus and its derivative. We used the experimental bulk modulus of Ni$_3$Al, B=174 GPa. [46] For B' we used the calculated value B'=5.2.

[44] B. Efron and R.J. Tibshirani, *An Introduction to the Bootstrap* (Chapmann and Hall, New York, 1993).

[45] C.J. Schinkel, F.R. de Boer, and B. de Hon, J. Phys. F **3**, 1463 (1973).

[46] F. Wallow, G. Neite, W. Schroer and E. Nembach, Phys. Status Solidi A **99**, 483 (1987).